Observation of liquidlike correlations of polyelectrolytes under high-shear conditions

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Angular static light scattering peaks were observed for a polyelectrolyte (Proteoglycan subunit) under elution in pure water in a size exclusion chromatography (SEC) system. The shear rates involved in the SEC experiments were fairly high. The peaks were quite comparable to those found under stationary (non-SEC) conditions, adding strength to the notion that dynamic, liquidlike correlations are the origin of such peaks observed for simple polyelectrolytes at low ionic strength.

Over the past few years an increasing number of observations of angular static and dynamic light scattering peaks have been made for several different linear and simply branched polymers at extremely low volume fractions and ionic strengths. Although not unanimously accepted, the simplest explanation for these peaks is that electrostatically enhanced volumes of the polyelectrolytes at low hard volume concentration lead to high effective volume concentrations, from which liquidlike correlations arise. Such correlations involve particles in rapid diffusive motion which avoid each other’s vicinity due to the electrostatic barrier.

The current note provides observations, for the first time to the author’s knowledge, of angular static light scattering peaks for a simply branched polyelectrolyte under the relatively high shear conditions of size exclusion chromatography (SEC) flow. These peaks are quite similar to those found for the system when left stationary for many hours, implying that the mechanism behind the peak is independent of shear stresses.

Proteoglycan subunits (or monomers) PGM, from bovine nasal cartilage were a gift from Dr. Anna Plaas (Shriver’s Hospital, FL). They have been extensively characterized over the last two decades as to chemical composition, structure, etc. Basically, they consist of a protein backbone from several thousand to about 20,000. Typical contour lengths of the PGM are around 4000 Å, making them much shorter (and less anisotropic) than linear polyelectrolytes of similar mass.

The SEC system consisted of a Waters 150C injector and RI detector, with a Hewlett Packard series 1050 pump in place of the Waters stock pump. The pump was run at a rate of 1 cm³/min in this work. The columns were Shodex 804 and 805 in series. The columns fed into a Wyatt Dawn-F multi-angle laser light scattering detector (MALLS), which then fed into the RI detector. The Dawn-F has 15 fixed scattering observation angles from 26°–156°, and used a vertically polarized helium–neon laser of wavelength λ = 6320 Å.

It has been described previously by its inventor and co-workers. The control and analysis software for the detector system (COUPLAGE) was written by the author. The Dawn-F allows a range of scattering vectors q = (4πn/λ)sin(θ/2) of 3.36 × 10⁻⁴ to 2.58 × 10⁻⁵ Å⁻¹ to be measured when water is the solvent (n = 1.33 being the index of refraction).

As a preliminary SEC characterization of the PGM, the SEC was eluted with a high ionic strength aqueous solution, 0.1 M NH₄NO₃, and a solution of PGM at concentration C_p = 0.0014 g/cm³ was injected into the injection loop of 0.2 cm³. The PGM was large enough that it eluted in the exclusion volume of the columns, so that minimal separation according to mass was achieved. The weight average mass M_w was around 1.8 million, where dn/dc = 0.147 was taken from Ref. 2. The z-averaged root-mean-square gyration radius R_g was around 500 Å. These values are comparable to those of Ref. 2. Some variation in the product, its polydispersities and mass distributions is normal from batch to batch.

The SEC system was then eluted and allowed to equilibrate overnight with ultrapure water from a Millipore Q purification system (conductivity less than 0.05 μS, outlet water filtered with a 0.22 μm filter). A PGM solution at C_p = 0.0014 g/cm³ was then injected. The flow rate was 1 cm³/min, and data were sampled every 2 s. The PGM again eluted in the exclusion volume, so that no appreciable separation according to mass occurred.

The angular intensity profile I(q) from the MALLS instrument showed a clear peak over the range of eluted concentrations, whose position and height were dependent on the concentration of PGM in each elution sample. Several of the peaked I(q) profiles, selected from hundreds in each chromatogram, are shown in Fig. 1(a). They are actually represented as I(q)/KC_p, where K is the optical scattering constant for vertically polarized incident light given by

\[ K = \frac{4\pi^2n^2(dn/dc)^2}{N_A\lambda^4}, \]

where N_A is Avogadro’s number. The concentrations in Fig.
Peaks in Ref. 2 are on the order of 10^{-5} g/cm^3. Hydrodynamic diameters $R_h$, of around 350 Å at no added salt conditions, extrapolated to $C_p=0$, were found for PGM in Ref. 2, so that the “hard” or “steric” volume fraction, estimated as $(4\pi R_h^3/3)C_pN_A/M_w$, is only around 0.06% at 10^{-3} g/cm^3.

Figure 1(b) shows typical monotonically decreasing $I(q)$ profiles from the PGM when eluted at high ionic strength, 0.1 M NH_4NO_3. The loss of the peak in going from no added salt [Fig. 1(a)] to high added salt [Fig. 1(b)] is a well-known characteristic of these scattering systems, and, in the liquid-like correlation interpretation is due to the collapse in the electrostatically enhanced effective volumes when salt is added and interparticle electrostatic repulsions are screened. In Ref. 2, it was sufficient to add NaCl to a concentration as low as 0.0003 M to eliminate the $I(q)$ peak and recover monotonically decreasing behavior for a 2.5·10^{-4} g/cm^3 solution of PGM.

The $I(q)$ curves in Fig. 1(a) are not appreciably different from those in Fig. 2 of Ref. 2, which were taken under static, no-flow conditions, using an Argon ion laser at $\lambda=4880$ Å. The peak widths from Fig. 1(a), defined as

$$\Delta q = \frac{\int I(q) dq}{I(q_p)}$$

are on the order of 10^{-3} Å^{-1}, the same as the widths for the no-flow peaks in Ref. 2. Here $q_p$ is the value of $q$ at the peak. Also, the height of $I(q)/Kc$ decreases with $C_p$ in Fig. 1(a), just as for the no-flow case of Ref. 2.

Plotting the interpolated peak scattering vector $q_p$ vs $C_p$ for two different SEC runs yields the log–log plot of Fig. 2. The peaks are located by

$$q_p(Ang^{-1})=0.001 06C_p^{0.375}(g/cm^3 \times 10^5).$$

Reference 2 gives a similar scaling, with the exponent of $C_p$ equal to 1/3. This scaling is consistent with a cubic three-dimensional disposition of Bragg-type scatterers. This does not imply any type of static, long-range order, however, merely that at any time there are strong, exclusive, neighbor–neighbor correlations with an average distance between them related to the inverse cubic root of $C_p$.

In Ref. 2, $\Delta q$ was interpreted in terms of the “Guinier disorder parameter.” The breadth of $\Delta q$ suggested that the PGM undergo very large root-mean-square displacements from their average separation.

The laminar flow in the SEC tubes is well approximated by Poiseuille type flow. As such, the shear rate $\dot{\gamma}(r)=dv(r)/dr$, at a distance $r$ from the center of the tube of inner radius $R$, and at a volume flow rate $Q$ (cm^3/s) is given by

$$\dot{\gamma}=-4Qr/\pi R^4.$$ 

The maximum occurs at the edge of the tube and is given by

$$\dot{\gamma}_{max}=-4Q/\pi R^3.$$ 

Within the Dawn-F flow cell, which has $R=0.12$ cm, $\dot{\gamma}_{max}$ is around 12 s^{-1}, whereas within the smallest tubes in the SEC system (where inner radius is around 0.02 cm) $\dot{\gamma}_{max}$ is around 2500 s^{-1}. Shear rates within the SEC columns may be even higher.

At a given flow rate, one can approximate the time it takes for two adjacent, small cubic volumes to pass each other due to the shear flow as $1/\dot{\gamma}$. “Small” here means that the cubes’ edge length $d$, is much smaller than $R$. This applies to “cubic cells” containing individual PGM, which should have $d=O(1 \mu m)$. Within the Dawn-F flow cell this time is on the order of 80 ms, whereas within the smaller tubes in the system it is on the order of 50 μs. Hence, the shear rates involved in these observations should be such that the PGMs move differentially past each other quite quickly and are thus prevented from forming any type of static, long-range organization on the time scale of the SEC experiment.

![Graph of $q_p$ vs $C_p$](image_url)
The similarity of the peaks observed under stationary (Ref. 2) and under flow (SEC) conditions lends strength to the earlier drawn conclusions that the origin of the scattering peaks is in liquidlike correlations between PGM particles. In this interpretation, the PGM have very large effective volumes $C_{v, \text{eff}}$ (much larger than the "hard" volume occupied by the PGM), due to high electrostatic repulsion at extremely low ionic strength, which leads to strong mutually avoiding correlations between nearest neighbors. The simplest such model, a spherical square well potential whose radius is the effective electrostatic radius $R_e$, predicts a structure function of the form

$$S(2qR_e) = 1 - 24C_v J_1(2qR_e)/2qR_e,$$

where $C_v$ is the effective volume fraction of the particles and $J_1(2qR_e)$ is the first order spherical Bessel function, which manifests rapidly damped oscillations. Although no secondary peaks were observed in the MALLS spectra from the SEC, there could be very weak secondary and higher order maxima at values of $q$ higher than the Dawn-F range, due to attenuated correlations between second-nearest neighbor and further neighbors.

In Ref. 2, the form factor $P(q)$ for PGM at no added salt was determined experimentally, from which $S(q)$ was determined via $S(q) = I(q)/P(q)$. $S(q)$ retained its peak after dividing $I(q)$ by $P(q)$.

We contrast the existence of the peaks in Fig. 1(a) with the type of more strongly defined peaks that exist in, e.g., solutions of latex spheres, which require hours or even days for the peak definition to set in strongly, and which form genuine long-range ordered systems, easily destroyed by small shear stresses. The current results are consistent with dynamic liquidlike correlations of highly diffusive individual PGM particles. It is unnecessary to invoke the idea, and in fact it is improbable under these high shear conditions, that the peaks are due to long range ordering of PGM particles or to the existence of delicate or fleeting "micro-domains."

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5 I. Morfin, W. F. Reed, M. Rinaudo, and R. Borsali, J. Physique II (in press).